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(54) OLIGOMERIZATION AND CATALYSTS THEREFOR

OLIGOMERISIERUNG UND KATALYSATOR DAFUER

OLIGOMERISATION ET CATALYSEURS UTILISES A CETTE FIN

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Description

This invention relates to oligomerization reactions, and to catalysts, more especially to molecular sieve, preferably zeolite, catalysts, and their use in such reactions.

Molecular sieve catalysts of many types have been proposed for use in numerous chemical processes. Among such processes are oligomerization reactions, especially of lower olefins, e.g., alkenes, to higher olefins, e.g., higher alkenes, for example, the oligomerization of C_2 to C_6, especially C_3 and C_4, olefins, to olefins in the C_6 to C_{12} range.

GB-A-2106131 describes oligomerizing medium molecular weight α-olefins, e.g., C_8 to C_{14} olefins, to form heavy olefin mixtures comprising trimers, tetramers and pentamers of the starting materials, using intermediate (0.5 to 0.65 nm) pore size zeolites or other molecular sieves as catalysts. As examples of zeolites are given HZSM-5, 11, 12, 21, 23, 35, and 38, and "crystalline admixtures" or physical admixtures of such zeolites, e.g., ZSM-5 and ZSM-11. U.S. Patent No. 4417086 has a similar disclosure.

U.S. Patent No. 4324940 describes, inter alia, the use as an oligomerization catalyst of ZSM-5, selectively oligomerizing smaller rather than larger molecules.

U.S. Patent No. 4642404 describes the activation of an extrudate of the medium pore zeolites listed in GB-A-2106131 with steam and the resulting activity of a ZSM-5 product treated in this way as a propene oligomerization catalyst. US patent No. 4754096 describes the oligomerization of propene using ZSM-5 to provide lubricant oil range hydrocarbons.

U.S. Patent No. 4975401 describes the advantage of using a mixture of ZSM-5 and ZSM-12 in cracking alkyl-benzenes over the use of either catalyst alone.

U.S. Patent No. 5177282 describes oligomerization of an olefin by passing it over two molecular sieves in series before being contacted with a Ni-containing catalyst; in an example ethene is passed first over a 0.3 nm pore size sieve, then over a Type 13X molecular sieve.

EP-A-293914 describes crystalline admixtures and physical mixtures of various molecular sieves and their use in oligomerization of olefins; in one example the catalytic activities of a SAPO-11/$AlPO_4$-11 composite and physical mixtures of the two sieves are compared.

U.S. Patent No. 4919898 describes the use of series reactors for oligomizeration of olefins; a number of different zeolites are proposed as catalysts.

U.S. Patent No. 4032432 relates primarily to cracking, but light ends withdrawn from the reactor are contacted with a catalyst comprising a mixture of larger pore, e.g., faujasite, and smaller pore, e.g., mordenite, erionite or ZSM-5, zeolites.

U.S. Patent No. 4247416 describes the preparation of ZSM-25 and mentions the possibility of its being incorporated in another unspecified zeolite as matrix.

All prior published proposals for olefin oligomerization have their advantages and disadvantages, the latter including an insufficient ability to control the extent of oligomerization. For example, in the oligomerization of propene, if ZSM-5 is employed as catalyst, the oligomer product contains a relatively low proportion of dimer, and higher proportions of trimer, tetramer and pentamer. If ZSM-22 is employed as catalyst, the dimer is by far the major product. However, in neither case is the yield of trimer high. If, therefore, the desired product is one with a high nonene content neither catalyst offers an attractive route.

The present invention is based on the observation that the product obtained when oligomerization is carried out over a catalyst comprising at least two molecular sieves contains a higher proportion of a certain oligomeric species than is obtainable by carrying out the reaction over any one of the zeolite species alone

In a first aspect, the invention provides a process for the oligomerization of an olefin, which comprises contacting under oligomerization conditions a feed comprising at least one olefin with a catalyst comprising at least one molecular sieve having a refined constraint index (as hereinafter defined) greater than 10 and at least one molecular sieve having a refined constraint index within the range of from 2 to 10 and recovering a product comprising at least one olefin oligomer.

The refined constraint index, CI°, is defined in J.A. Martens, M. Tielen, P.A. Jacobs and J. Weitkamp, Zeolites, 1984, p. 98, and P.A. Jacobs & J.A. Martens, Pure and Applied Chem., 1986, Vol. 58, p. 1329, as the ratio of 2-methylnonane to 5-methylnonane produced at 5% conversion in the hydro-isomerization of n-decane.

Examples of molecular sieves having a CI° greater than 10 include ZSM-22, ZSM-23, and certain ferrierites. Examples of molecular sieves having a CI° between 2 and 10, inclusive, include ZSM-5, 11, 12, 35, 38, 48, and 57, SAPO-11, MCM-22 and erionite, those having a CI° between 5 and 10 presently being preferred.

It is within the scope of the invention to employ mixtures containing two or more molecular sieves having a CI° of one type with one or more molecular sieves of the other type.

The molecular sieve or zeolite catalysts are advantageously ZSM-5, and ZSM-22 and ZSM-57. Zeolite ZSM-5 is described in U.S. Patent No. 3702886 and in WO 93/25476, ZSM-22 is described in U.S. Patent No. 4556477 and in WO 93/25475, and ZSM-57 is described in EP-A-174121 and U.S. Patent No. 4973781, the disclosures of all of which

are incorporated herein by reference.

In a second aspect, the invention provides a process for the oligomerization of an olefin, which comprises contacting under oligomerization conditions a feed comprising at least one olefin with a zeolite catalyst comprising ZSM-5 and ZSM-22 and recovering a product comprising at least one olefin oligomer.

A molecular sieve crystallite size advantageously up to 5 μm, preferably within the range of from 0.05 to 5 μm, more especially from 0.05 to 2 μm, and most preferably from 0.1 to 1.0 μm, may be employed.

The as-synthesized molecular sieves are advantageously converted to the acid form, generally by acid treatment, for example by HCl, or by ammonium ion exchange, and subsequent calcination. The sieves may be post-treated, as by steaming, or may be caused to contain other cations either by incorporation during preparation or by subsequent ion-exchange, examples of suitable cations being Ni, Cd, Cu, Zn, Pd, Ca, Ga, B and Ti and rare earth metals.

The two sieves are advantageously present in the catalyst in proportions by weight of 10:90 to 90:10, especially from 20:80 to 80:20, more especially from 25:75 to 75:25, for example 50:50. The optimum ratio will depend on the activity of each catalyst, with a less active component being present in a greater proportion than a more active. Accordingly, for example, since ZSM-57 appears to be more active than ZSM-5, the ZSM-57/22 ratio for an optimum trimerization of C_3 olefin may be lower than the ZSM-5/22 ratio. For a feed containing C_4 or above olefin, it is advantageous for the ZSM-22 to be present in a major proportion in a ZSM-5/ZSM-22 mixture. For a feed containing C_3 olefin, ZSM-5 should predominate when a C_9 olefin oligomer is desired.

It is within the scope of the invention for the two molecular sieves to be separate, so that the feed passes through them in series, e.g., in the form of stacked catalyst beds or reactors in series. In this case, it is advantageous for the catalyst with CI° greater than 10, e.g., ZSM-22, to be upstream of the catalyst with CI° between 2 and 10, e.g., ZSM-5 or -57 in a ZSM-5/ZSM-22 or ZSM-57/ZSM-22 combination.

Advantageously, however, the two sieves are in admixture. They may be used in the form of a homogeneous crystalline admixture, a homogeneous powder mixture, a homogeneous extrudate, or as a mixed extrudate. The extrudate advantageously contains the molecular sieves, especially the zeolites, in the desired relative proportions as indicated above, and a binder, for example alumina, silica, an aluminosilicate; or clay, advantageously in a proportion of from 10:90 to 90:10, preferably 20:80 to 80:20, by weight of total zeolite to binder. The sieves and binder may be composited by, for example, intimately mixing them together in the presence of water, and extruding or otherwise shaping, e.g., by pelletizing.

The feed olefin advantageously contains from 2 to 12 carbon atoms, and preferably from 2 to 6 carbon atoms; more preferably, the olefin feed advantageously contains propene, butenes and/or pentenes.

Reaction conditions for the oligomeration process of the invention may be, with the exception of the use of the dual catalyst, in accordance with conditions operative for prior art processes oligomerizing the same olefin.

The olefin may, for example, be fed to the catalyst in admixture with an inert diluent, e.g., a saturated hydrocarbon, in the liquid or, preferably, the gaseous, phase. For a feed comprising propene, a suitable diluent is propane, advantageously in proportions of propene:propane from 10:90 to 60:40, especially about 50:50 by weight. The feed is advantageously hydrated; preferably it contains from 0.05% to 2% by weight water. The desired proportion of water may be incorporated by saturating the feed at an appropriate temperature, e.g., from 25 to 60°C, or by injecting water through a pump.

The oligomerization may take place at a temperature advantageously in the range of from 170°C to 300°C, preferably from 170°C to 260°C, and most preferably from 180°C to 260°C, at a pressure advantageously in the range of from 5 to 10 MPa, preferably from 6 to 8 MPa, and at an olefin hourly space velocity advantageously in the range 0.1 to 20, preferably from 1 to 10, and most preferably 1.5 to 7.5, whsv.

As will be apparent from the results below, the present invention makes possible a wider choice of product mix than is available by oligomerization using a single catalyst. Accordingly, the invention also provides the use in an olefin oligomerization reaction of a two molecular sieve catalyst system, especially a ZSM-5/ZSM-22 catalyst system, to control the oligomer product distribution.

The invention further provides the use of a two molecular sieve catalyst system, especially a ZSM-5/ZSM-22 system, to control, more especially to maximize, the proportion of nonenes resulting from the oligomerization of propene.

The present invention still further provides a process for the manufacture of a nonene-containing product, which comprises contacting a propene-containing feedstock under oligomerization conditions with a molecular sieve catalyst comprising ZSM-5 and ZSM-22.

The invention further provides an admixture of ZSM-5 and ZSM-22 zeolites in the form of an extrudate and an admixture of ZSM-57 and ZSM-22 zeolites, in each case advantageously in proportions of 10:90 to 90:10 by weight.

It has surprisingly been found that the catalyst mixtures have greater stability, in the sense of retaining their oligomerization catalytic activity, than the component catalysts alone. The invention accordingly also provides the use of the molecular sieve catalyst mixtures to enhance catalyst activity retention.

The following examples, in which parts and percentages are by weight unless otherwise stated, illustrate the invention:

In the Examples 1 to 15, the two zeolites used, ZSM-5 (CI° 6.8) and ZSM-22 (CI° 14.4), were both received from the manufacturer as powders in calcined and acidic form. The ZSM-5 had a SiO_2/Al_2O_3 ratio of about 35:1, and a crystallite size of 0.1 to 0.8 μm. Homogeneous powder materials were prepared as follows:

Sample	% ZSM-22	%ZSM-5
A	100	0
B	75	25
C	50	50
D	25	75
E	0	100

Oligomerizations were carried out under the following conditions:

Feed:
50% by weight propene in propane
Total Feed Space Velocity:
2 wt/wt.h
Feed Hydration:
at 40°C
Pressure:
7 MPa

Each reaction was commenced at a temperature within the range of 195 to 205°C, and a conversion of 85% propene or higher was maintained by adjustment of reaction temperature. Conversion product selectivity and quality (degree of branching, see below) were analysed by off-line gas chromatography.

Examples 1 to 3 and Comparative Examples 1 & 2

Condition: 90% propene conversion.

Example	Sample	Product Selectivity - Alkenes of C number shown			
		C_6	C_9	C_{12}	C_{15}^+
Comp 1	A	59	26	8	3
1	B	34	43	14	5
2	C	13	51	18	9
3	D	8	51	20	10
Comp 2	E	4	36	23	16

The results clearly show that using pure ZSM-22, Comparative Example 1, or pure ZSM-5, Comparative Example 2, the maximum selectivity for nonenes is limited to 36. Using a mixed catalyst according to the invention, nonene selectivity is raised to 51.

In contrast, the selectivities for C_6, C_{12} and C_{15+} of the mixtures are substantially linear progressions between the pure zeolites. While the applicants do not wish to be bound by any theory, it appears that in the mixed catalyst examples hexenes produced by ZSM-22 are converted in situ by ZSM-5 by reaction with propene to the desired nonenes.

The degrees of branching of the nonenes produced by the catalysts were measured.

Catalyst mixture	Propene conversion %	linear	Isomeric Content % mono	di	tri	Degree of Branching
A	92.4	0.09	34.56	54.35	10.59	1.75
B	88.0	1.82	21.11	68.44	8.63	1.84
C	89.0	0.98	13.11	77.86	8.05	1.93
D	91.8	0.93	12.78	78.34	7.96	1.93
E	91.5	0	8.52	83.39	9.09	2.01

The degree of branching for Samples B to D ranges between the values for the pure catalysts, and the proportions of mono and di branched isomers produced by the mixtures also make linear progressions.

Examples 4 to 15

In these Examples, the effect of varying propene conversion on the degree of branchiness was investigated for catalyst mixtures B, C and D.

Example	Catalyst mixture	Propene conversion %	linear	Isomeric Content % mono	di	tri	Degree of Branching
4	B	100	1.98	27.42	63.15	7.46	1.76
5		94.1	2.12	25.96	65.00	6.92	1.77
6		88.0	1.82	21.11	68.44	8.63	1.84
7		84.6	0.21	21.43	69.20	9.16	1.87
8	C	100	0.0	27.66	65.52	8.82	1.81
9		99.0	0.0	18.38	74.45	7.17	1.89
10		95.8	1.38	18.89	72.82	6.92	1.85
11		89.0	0.98	13.11	77.86	8.05	1.93
12	D	100	2.12	27.92	58.17	11.79	1.80
13		98.2	1.30	17.34	73.88	7.48	1.88
14		91.8	0.93	12.78	78.34	7.96	1.93
15		78.7	0.80	10.38	80.48	8.34	1.96

The results show that the degree of branching is influenced by the conversion rate, the proportion of di-branching falling, and that of mono-branching rising, as conversion rate approaches 100% in all cases.

Example 16 and Comparative Examples 3, 4 and 5

In these Examples ZSM-22 and ZSM-57 (CI° 2.0) were used. Oligomerizations were carried out under the following conditions:

Feed:
12% by weight propene in propane
Temperature:
245°C
Propene Space Velocity (WHSV):
See Table
Pressure:
6.8 MPa

The results are shown in the Table below.

Example	Ratio ZSM-22: ZSM:57	Propene WHSV	Propene Conv.,%	Product C_6	Product C_9	Selectivity % C_{12}	Selectivity % C_{15}^+
Comp 3	100:0	4.5	92	56	27	9	3
16	50:50	5.6	94	18	34	17	12
Comp 4	0:100	8	95	10	24	20	20
Comp 5	0:100	3.7	94	8	27	21	24

Activation: Comp. 3: Calcination at 400°C in air; Example 16 and Comps. 4 and 5: ammonium exchange followed by calcination in air at 400°C.

The mixed catalyst also has a greater stability, as shown by its ability to maintain a high propene conversion for long periods on stream.

Example	g. propene per g. catalyst 30	45	60	100	125	150
Comp 3	97	98.6	98.3	96.6	93.5	---
16	99.5	99.4	99.3	99.0	96.5	93.2
Comp 5	100	81	58	---	---	---

Comparative Examples 6 to 8

In these Examples, ZSM-22 and zeolite Beta (CI° 1.4) were used, alone and in admixture. Oligomerizations were carried out under the following conditions:

Feed: see Table
Temperature: 200°C
Propene Space Velocity: see Table
Pressure: 6.8 MPa

The results are shown in the Table below:

Example	ZSM-22: Beta	Propene WHSV	% Propene in propane	Propene Conv.,%	Product Selectivity % C_6	C_9	C_{12}	C_{15^+}
Comp 6	100:0	20	50	94	49	28	12	7
Comp 7	75:25	19	50	94	29	27	18	15
Comp 8	0:100	8	12*	91	10	15	21	21

* Comp. 8, using 100% Zeolite Beta was carried out at 12% propene content because of the low time-on-stream stability of pure H-Beta. As is apparent from the results, product selectivity of the mixture was between those of the two pure zeolites. This was also true of the stability.

Claims

1. A process for the oligomerization of an olefin, which comprises contacting under oligomerization conditions a feed comprising at least one olefin with a catalyst comprising at least one molecular sieve having a refined constraint index (CI°) greater than 10 and at least one molecular sieve having a CI° within the range of from 2 to 10 and recovering a product comprising at least one olefin oligomer.
2. A process as claimed in claim 1, wherein the catalyst comprises ZSM-22 and ZSM-5.
3. A process as claimed in claim 1, wherein the catalyst comprises ZSM-22 and ZSM-57.
4. A process as claimed in any one of claims 1 to 3, wherein the feed olefin contains from 2 to 12 carbon atoms.
5. A process as claimed in any one of claims 1 to 4, wherein the feed olefin contains from 2 to 6 carbon atoms.
6. A process as claimed in any one of claims 1 to 4, wherein the feed olefin is propene.
7. A process as claimed in any one of claims 1 to 6, wherein the olefin feed contains a butene and/or a pentene.
8. A process as claimed in any one of claims 1 to 7, wherein the catalyst contains two molecular sieves in a proportion within the range of from 10:90 to 90:10 by weight.
9. A process as claimed in any one of claims 1 to 8, wherein the olefin feed passes through the two molecular sieves of the catalyst in series.
10. A process as claimed in claim 9, wherein the catalysts include ZSM-22, and the ZSM-22 is upstream of ZSM-5 or ZSM-57.
11. A process as claimed in any one of claims 1 to 8, wherein the catalyst comprises two molecular sieves in admixture.

12. A process as claimed in claim 11, wherein the catalyst comprises molecular sieves in a crystalline admixture.

13. A process as claimed in claim 11, wherein the catalyst is in the form of a powder mixture.

14. A process as claimed in claim 11 or claim 12, wherein the catalyst is in the form of an extrudate.

15. A process as claimed in any one of claims 1 to 14, wherein the olefin is fed to the catalyst in admixture with an inert diluent.

16. A process as claimed in any one of claims 1 to 15, wherein the olefin feed is hydrated.

17. A process as claimed in any one of claims 1 to 16, carried out at a reactant space velocity of from 1.5 to 7.5 whsv.

18. A process as claimed in claim 1 for the manufacture of a nonene-containing product, which comprises contacting a propene-containing feedstock under oligomerization conditions with a catalyst comprising ZSM-5 and ZSM-22.

19. The use in an olefin oligomization reaction of a molecular sieve catalyst system comprising at least one molecular sieve having a CI° greater than 10 and at least one molecular sieve having a CI° within the range of 2 to 10, to control the oligomer product distribution.

20. The use of a two molecular sieve catalyst system, comprising at least one molecular sieve having a CI° greater than 10 and at least one molecular sieve having a CI° within the range of 2 to 10, to control, more especially to maximize, the proportion of nonenes resulting from the oligomerization of propene.

21. The use of a two molecular sieve catalyst system comprising at least one molecular sieve having a CI° greater than 10 and at least one molecular sieve having a CI° within the range of 2 to 10, to enhance oligomerization catalytic activity stability.

22. An admixture of ZSM-5 and ZSM-22 zeolites in the form of an extrudate

23. An admixture of ZSM-57 and ZSM-22 zeolites.

24. An admixture as claimed in claim 22 or claim 23, in proportions of from 10:90 to 90:10 by weight

Patentansprüche

1. Verfahren zum Oligomerisieren von Olefin, bei dem unter Oligomerisierungsbedingungen ein Einsatzmaterial, das mindestens ein Olefin umfaßt, mit einem Katalysator kontaktiert wird, der mindestens ein Molekularsieb mit einem Feinrestriktionsindex (CI°) von mehr als 10 und mindestens ein Molekularsieb mit einem CI° im Bereich von 2 bis 10 umfaßt, und ein Produkt gewonnen wird, das mindestens ein Olefinoligomer umfaßt.

2. Verfahren nach Anspruch 1, in dem der Katalysator ZSM-22 und ZSM-5 umfaßt.

3. Verfahren nach Anspruch 1, bei dem der Katalysator ZSM-22 und ZSM-57 umfaßt.

4. Verfahren nach einem der Ansprüche 1 bis 3, bei dem das Einsatzolefin 2 bis 12 Kohlenstoffatome enthält.

5. Verfahren nach einem der Ansprüche 1 bis 4, bei dem das Einsatzolefin 2 bis 6 Kohlenstoffatome enthält.

6. Verfahren nach einem der Ansprüche 1 bis 4, bei dem das Einsatzolefin Propen ist.

7. Verfahren nach einem der Ansprüche 1 bis 6, bei dem das Einsatzolefin Buten und/oder Penten enthält.

8. Verfahren nach einem der Ansprüche 1 bis 7, bei dem der Katalysator zwei Molekularsiebe in einem Anteil im Bereich von 10:90 bis 90:10 enthält, bezogen auf das Gewicht.

9. Verfahren nach einem der Ansprüche 1 bis 8, bei dem das Olefineinsatzmaterial die beiden Molekularsiebe des Katalysators in Reihe passiert.

10. Verfahren nach Anspruch 9, bei dem die Katalysatoren ZSM-22 einschließen und das ZSM-22 stromaufwärts von ZSM-5 oder ZSM-57 ist.

11. Verfahren nach einem der Ansprüche 1 bis 8, bei dem der Katalysator eine Mischung aus zwei Molekularsieben umfaßt.

12. Verfahren nach Anspruch 11, bei dem der Katalysator Molekularsiebe in einer kristallinen Mischung umfaßt.

13. Verfahren nach Anspruch 11, bei dem der Katalysator in Form einer Pulvermischung vorliegt.

14. Verfahren nach Anspruch 11 oder Anspruch 12, bei dem der Katalysator in Form eines Extrudats vorliegt.

15. Verfahren nach einem der Ansprüche 1 bis 14, bei dem das Olefin dem Katalysator gemischt mit einem inerten Verdünnungsmittel zugeführt wird.

16. Verfahren nach einem der Ansprüche 1 bis 15, bei dem das Olefineinsatzmaterial hydratisiert ist.

17. Verfahren nach einem der Ansprüche 1 bis 16, das mit einer Reaktant-Raumgeschwindigkeit von 1,5 bis 7,5 WHSV durchgeführt wird.

18. Verfahren nach Anspruch 1 zur Herstellung eines nonenhaltigen Produkts, bei dem ein propenhaltiges Einsatzmaterial unter Oligomerisierungsbedingungen mit einem Katalysator kontaktiert wird, der ZSM-5 und ZSM-22 umfaßt.

19. Verwendung eines Molekularsiebkatalysatorsystems, das mindestens ein Molekularsieb mit einem CI° von mehr als 10 und mindestens ein Molekularsieb mit einem CI° im Bereich von 2 bis 10 umfaßt, in einer Olefinoligomerisierungsreaktion zur Steuerung der Oligomerproduktverteilung.

20. Verwendung eines Katalysatorsystems aus zwei Molekularsieben, das mindestens ein Molekularsieb mit einem CI° von mehr als 10 und mindestens ein Molekularsieb mit einem CI° im Bereich von 2 bis 10 umfaßt, zur Steuerung, insbesondere zur Maximierung des Anteils von Nonenen, die aus der Oligomerisierung von Propen resultieren.

21. Verwendung eines Katalysatorsystems aus zwei Molekularsieben, das mindestens ein Molekularsieb mit einem CI° von mehr als 10 und mindestens ein Molekularsieb mit einem CI° im Bereich von 2 bis 10 umfaßt, zur Erhöhung der Stabilität der katalytischen Oligomerisierungsaktivität.

22. Mischung aus ZSM-5 und ZSM-22 Zeolithen in Form eines Extrudats.

23. Mischung aus ZSM-57 und ZSM-22 Zeolithen.

24. Mischung nach Anspruch 22 oder Anspruch 23 in Anteilen von 10:90 bis 90:10, bezogen auf das Gewicht.

Revendications

1. Procéde d'oligomérisation d'une oléfine, qui comprend les étapes consistant à mettre en contact, dans des conditions d'oligomérisation, une charge comprenant au moins une oléfine avec un catalyseur comprenant au moins un tamis moléculaire ayant un indice de contrainte (CI°) raffiné supérieur à 10 et au moins un tamis moléculaire ayant un CI° dans la plage de 2 à 10, et à recueillir un produit contenant au moins un oligomère d'oléfine.

2. Procédé suivant la revendication 1, dans lequel le catalyseur comprend les tamis moléculaires ZSM-22 et ZSM-5.

3. Procédé suivant la revendication 1, dans lequel le catalyseur comprend les tamis moléculaires ZSM-22 et ZSM-57.

4. Procédé suivant l'une quelconque des revendications 1 à 3, dans lequel l'oléfine constituant la charge contient 2 à 12 atomes de carbone.

5. Procédé suivant l'une quelconque des revendications 1 à 4, dans lequel l'oléfine constituant la charge contient 2 à 6 atomes de carbone.

6. Procédé suivant l'une quelconque des revendications 1 à 4, dans lequel l'oléfine constituant la charge est le propène.

7. Procédé suivant l'une quelconque des revendications 1 à 6, dans lequel la charge oléfinique contient un butène et/ou un pentène.

8. Procédé suivant l'une quelconque des revendications 1 à 7, dans lequel le catalyseur contient deux tamis moléculaires dans une proportion comprise dans la plage de 10:90 à 90:10 en poids.

9. Procédé suivant l'une quelconque des revendications 1 à 8, dans lequel la charge oléfinique passe à travers les deux tamis moléculaires du catalyseur en série.

10. Procédé suivant la revendication 9, dans lequel les catalyseurs comprennent le tamis moléculaire ZSM-22. et celui-ci est en amont de ZSM-5 ou ZSM-57.

11. Procédé suivant l'une quelconque des revendications 1 à 8, dans lequel la catalyseur comprend deux tamis moléculaires en mélange.

12. Procédé suivant la revendication 11, dans lequel le catalyseur comprend des tamis moléculaires en mélange cristallin.

13. Procédé suivant la revendication 11, dans lequel le catalyseur est sous forme d'un mélange en poudre.

14. Procédé suivant la revendication 11 ou la revendication 12, dans lequel le catalyseur est sous forme d'un extrudat.

15. Procédé suivant l'une quelconque des revendications 1 à 14, dans lequel l'oléfine arrive au contact du catalyseur en mélange avec un diluant inerte.

16. Procédé suivant l'une quelconque des revendications 1 à 15, dans lequel la charge oléfinique est hydratée.

17. Procédé suivant l'une quelconque des revendications 1 à 16, mis en oeuvre à une vitesse spatiale des corps réactionnels de 1,5 à 7,5 en vitesse spatiale horaire en poids.

18. Procédé suivant la revendication 1 pour l'obtention d'un produit contenant du nonène, qui comprend la mise on contact d'une charge d'alimentation contenant du propène dans des conditions d'oligomérisation avec un catalyseur comprenant les tamis moléculaires ZSM-5 et ZSM-22.

19. Utilisation, dans une réaction d'oligomérisation d'oléfine, d'un système catalyseur à base de tamis molèculaires comprenant au moins un tamis moléculaire ayant un indice CI° supérieur à 10 et au moins un tamis moléculaire ayant un indice CI° compris dans la plage de 2 à 10, pour infleur sur la distribution du produit oligomère.

20. Utilisation d'un système de catalyseur contenant deux tamis moléculaires, comprenant au moins un tamis moléculaire ayant un indice CI° supérieur à 10 et au moins un tamis moléculaire ayant un indice CI° dans la plage de 2 à 10, pour influer sur, et plus spécialement pour maximiser, la proportion de nonènes résultant de l'oligomérisation de propène.

21. Utilisation d'un système de catalyseur à deux tamis moléculaires comprenant au moins un tamis moléculaire ayant un indice CI° supérieur à 10 et au moins un tamis moléculaire ayant un indice CI° compris dans la plage de 2 à 10, pour améliorer la stabilité de l'activité catalytique d'oligomérisation.

22. Mélange de zéolites ZSM-5 et ZSM-22 sous forme d'un extrudat.

23. Mélange de zéolites ZSM-57 et ZSM-22.

24. Mélange suivant la revendication 22 ou la revendication 23 dans des proportions de 10:90 à 90:10 en poids.